PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: H01L 21/205
A1
(11) International Publication Number: WO 00/63957
(43) International Publication Date: 26 October 2000 (26.10.2000)

(21) International Application Number: PCT/KR00/00310
(22) International Filing Date: 06 April 2000 (06.04.2000)
(30) Priority Data:
1999/11877 06 April 1999 (06.04.1999) KR
(60) Parent Application or Grant
GENITECH, INC. [/]; (). LEE, Chun-Soo [/]; (). KANG, Won-Gu [/]; (). LEE, Kyu-Hong [/]; (). YI, Kyoung-Soo [/]; (). LEE, Chun-Soo [/]; (). KANG, Won-Gu [/]; (). LEE, Kyu-Hong [/]; (). YI, Kyoung-Soo [/]; (). HUH, Jin-Seok ; ().

Published

(54) Title: METHOD OF FORMING A THIN FILM
(54) Titre: PROCEDE DE FORMATION D'UN FILM MINCE

(57) Abstract

The invention provides a method of forming a thin film for semiconductor or flat panel display devices. In a chemical vapor deposition method which supplies cyclically reactant gases and a purge gas which prevents the gas-phase reaction between the reactant gases, generating plasma on a substrate synchronously with the gas supply cycle can form a thin film at low temperature and reduce particle generation at exhaust.

(57) Abrégé

L'invention concerne un procédé de formation d'un film mince pour afficheurs à semi-conducteur ou écrans à plasma. Selon un procédé de dépôt chimique en phase vapeur générant des gaz réactants cycliques et un gaz de purge évitant la réaction gaz-phase entre les gaz réactants, la génération de plasma sur un substrat en synchronisation avec le cycle d'alimentation du gaz peut former un film mince à une température basse et réduire la génération de particules lors de son échappement.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : H01L 21/205 — A1

(11) International Publication Number: WO 00/63957

(43) International Publication Date: 26 October 2000 (26.10.00)

(21) International Application Number: PCT/KR00/00310

(22) International Filing Date: 6 April 2000 (06.04.00)

(30) Priority Data:
1999/11877 6 April 1999 (06.04.99) KR

(71) Applicant *(for all designated States except US)*: GENITECH, INC. [KR/KR]; 1694-5 Sinil-dong, Taedok-ku, Taejon 306-230 (KR).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: LEE, Chun-Soo [KR/KR]; 109-202 Hanbit Apt., 99 Uheun-dong, Yusong-gu, Taejon 305-333 (KR). KANG, Won-Gu [KR/KR]; 118-908 Hanbit Apt., 99 Uheun-dong, Yusong-gu, Taejon 305-333 (KR). LEE, Kyu-Hong [KR/KR]; 105-606 Hanul Apt., 160-1 Shinsung-dong, Yusong-gu, Taejon 305-345 (KR). YI, Kyoung-Soo [KR/KR]; 118-1506 Hanbit Apt., 99 Uheun-dong, Yusong-gu, Taejon 305-333 (KR).

(74) Agent: HUH, Jin-Seok; J.S. Huh Patent Office, 206 Sungji Building, 1338-22 Seocho-dong, Seocho-ku, Seoul 137-070 (KR).

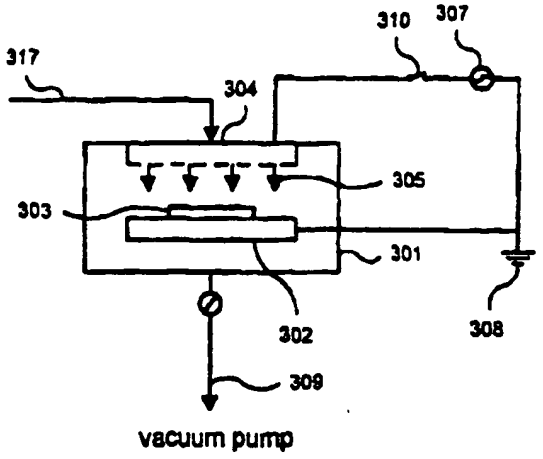
(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
In English translation (filed in Korean).

(54) Title: METHOD OF FORMING A THIN FILM

(57) Abstract

The invention provides a method of forming a thin film for semiconductor or flat panel display devices. In a chemical vapor deposition method which supplies cyclically reactant gases and a purge gas which prevents the gas-phase reaction between the reactant gases, generating plasma on a substrate synchronously with the gas supply cycle can form a thin film at low temperature and reduce particle generation at exhaust.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Description

METHOD OF FORMING A THIN FILM

TECHNICAL FIELD

The present invention relates to a deposition method of thin films required for manufacturing semiconductor devices. flat panel devices. and etc..

BACKGROUND ART

Such thin films may include metal films. insulator films such as metal oxide films. metal nitride films and etc.. films for capacitors. interconnects and electrodes, inorganic films used for diffusion prevention, and etc.

These thin films may be formed by a physical vapor deposition. for example a sputtering process. The sputtering process, however, forms thin films with poor step coverage, so a chemical vapor deposition method is usually employed to improve the step coverage.

One of the most common chemical vapor depositions of the prior art is carried out by an apparatus as shown in FIG. 1A. Referring to FIG. 1A, process gases or other reactants 11, 12, 13 are supplied into a reactor 1, respectively, through mass flow controllers 21, 22, 23 and valves 30, 31, 32. In this case, a shower head 4 is utilized to obtain uniform flow 5 of the process gases. When a source material is liquid or solid having low equilibrium vapor pressures, a vaporizer 16 is also employed that can heat the source material in a suitable temperature to vaporize and can supply the vaporized source material into the reactor 1 with the carrier gas 13. When the vaporizer is employed, the initial portion of the source material carried by the carrier gas 13 is exhausted via a bypass valve 33 and an outlet tube 18 due to the fluctuation of flow rate and source material concentration. Then, the bypass valve 33 is shut off and a valve 32 connected to a central supplying tube 17 is opened to supply the carrier gas into the reactor 1.

The chemical vapor deposition of the prior art performed in this apparatus has the following features: At first. all process gases 11, 12, 13 required for the deposition are supplied into the reactor 1 at the same time so that the film is continuously deposited during the process times 11', 12', 13' as in an example shown in FIG. 1B. At second, the shower head 4 is usually employed to make uniform flow

5 of the process gases on the surface of a substrate.

This method has the following disadvantages: At first, since all process gases exist within the reactor at the same time, the process gases may react in gas phase thereby can deteriorate step coverage of the deposited film and/or produce particles which contaminate the reactor. At second, when using a metal-organic compound as a source material, it is difficult to deposit the film that does not contain carbon impurities. At third, in the case of depositing a multi-component film, all the reactant materials must react simultaneously while the supply of each reactant material is controlled separately by mass flow of the carrier gas, so it is very difficult to control the composition of the deposited film precisely.

To overcome the foregoing problems, a method is proposed in which the process gases are supplied separately as time-divisional pulses rather than supplied continuously.

An example of supplying process gases in this deposition method is shown in FIG. 2A. Valves in a gas introducing part can be opened or closed so that the process gases can be supplied cyclically as time-divisional pulses into the reactor without being mixed with each other.

Referring to FIG. 2A, it can be seen that the process gases 11, 12, 13 in FIG. 1A are supplied in a cycle T_{cycle} of 13', 12', 11' and 12'. A film can be deposited by repeating this cycle. In general, purge gas 12 is supplied between the supply pulses of the reactants 11 and 13 so that the remaining reactants are removed from the reactor before the next reactant is supplied.

Hereinafter, a time-divisional deposition mechanism will be described. Chemical adsorption temperatures of the reactants onto the substrate are generally lower than thermal decomposition temperatures of the reactants. Therefore, when a deposition temperature is maintained higher than the chemical adsorption temperature of the reactant onto the substrate and lower than the thermal decomposition temperature of the reactant, the reactant supplied into the reactor only adsorbs chemically onto the surface of the substrate rather than decomposes. Then, the remaining reactant is exhausted out of the reactor by the purge gas supplied into the reactor. After that, another reactant is introduced into the reactor to react with the reactant adsorbed on the surface, and thus form a film. Because the reactant adsorbed

on the substrate cannot form more than one molecular layer, film thickness formed in one supply cycle T_{cycle} is constant regardless of amount or time of the supplied reactants. Therefore, as shown in FIG. 2B. the deposited film thickness is saturated as the supplying time elapses. In this case, the deposited film thickness is controlled only by the number of the repeated supply cycles.

In the other hand, when the deposition process temperature is no lower than the thermal decomposition temperature of the reactants, the deposited film thickness is proportional to the supply time of the reactants in the supply cycle because the reactants introduced into the reactor decompose continuously to form films on the substrate. In this case, deposited film thickness according to the supply time of the reactants is shown in FIG. 2C.

However, the foregoing time-divisional deposition has problems as follows:

At first, the reactants used in the deposition process must react readily. Otherwise it is difficult to form a film by time-divisional deposition. In this case, a method is required that facilitate the chemical reaction even at low temperatures.

At second, the exhausting part of the apparatus may be contaminated with particles due to the reactions between the reactants. The gas-introducing part and the reactor may not be contaminated with the particles due to the reactions of the reactants because the reactants are separated by the purge gas. In the other hand, the exhausting part may be easily contaminated with particles because the reactants mix and react with each other at exhaust.

At third, it is required to supply inert purge gas between the reactant supply pulses to prevent gas-phase reactions in the gas-introducing part and the reactor, so the gas-supply cycle is complex, the time for a supply cycle is longer than absolutely necessary, and thus the deposition is slow.

A method is disclosed in the US Patent No. 5,916,365 in which a film is formed by repeating a gas-supply cycle, i.e., supplying first reactant gas into a reactor, exhausting remaining reactant gas within the reactor by a vacuum pump, supplying second reactant gas which is activated by passing through a radical generator using an RF power or other means, and exhausting remaining reactant gas by the vacuum pump.

The exhaust rate of the vacuum pump decreases as the pressure decreases, so

it takes long time to exhaust the remaining reactant gases from the reactor with the vacuum pump. Therefore, in this method, it is difficult to have high growth rate of the film per unit time when it desired to exhaust the remaining reactant gases completely. When the exhausting time is too short, the reactant gases remain in the reactor so that the two reactant gases mix and react in gas phase. Furthermore, in the method of the US Patent No. 5,916,365, it is difficult to maintain stable plasma in the reactor because the supply and exhaust of the reactant gases cause wide pressure variation in the reactor.

DISCLOSURE OF INVENTION

Therefore, it is an object of the present invention to provide a method which can form a thin film effectively even if reactants do not react readily in a time-divisional source supply chemical vapor deposition method.

It is another object of the present invention to provide a method which can minimize supply time of a purge gas in a gas-supplying cycle to reduce cycle time in a time-divisional source supply chemical vapor deposition.

It is further object of the present invention to provide a method which can reduce particle contamination of the apparatus at the exhausting part of an apparatus for time-divisional source supply chemical vapor deposition.

In order to realize those foregoing objects, the present invention provides a method used for a chemical vapor deposition in which source gases for forming a thin film are supplied into a reactor in a time-divisional manner so that they may not be mixed with each other in the reactor. In the method of the invention, the process gases are activated into plasma to faciliate the film formation, wherein plasma is generated synchronously with gas supply cycle.

For more clear description, process gases are classified as three kinds:

At first, the process gas that thermally decomposes to form a solid film is called a deposition gas. The deposition gas includes, for example, titanium-organic compound used for chemical vapor deposition for forming a TiN film.

At second, the process gas that does not decompose by itself or does not form a solid film upon self-decomposition, however, forms a solid film when reacts with a deposition gas is called a reactant gas. The reactant gas includes, for example,

ammonia used in a chemical vapor deposition process for forming a nitride film, and oxygen gas used in a chemical vapor deposition process for forming a oxide film.

At third, the other inert process gas that is supplied between the supplies of the deposition gas and the reactant gas to separate the deposition gas and the reactant gas is called a purge gas. In general, helium, argon, nitrogen gas and etc. are used for a purge gas. Those gases contain the constituent element of the film may also used for a purge gases if they do not react with a deposition gas. In this case, the purge gas can be used for a reactant gas when activated by plasma.

Therefore, one of the most evident features of the present invention, in a chemical vapor deposition which forms a film on a substrate by supplying process gases which include a deposition gas, a reactant gas, and a purge gas into a reactor by repeating cycles of time-divisional gas supply, is to provide a method of generating plasma on the substrate synchronously with the supply cycles to activate at least one of the process gases. In this case, the plasma is generated synchronously with the supply cycle of the reactant gas.

Also, when a purge gas contains constituent elements of a film material and a reactant gas contains the other constituent elements of the film material and the purge gas does not substantially react with the reactant gas, plasma may be preferably generated synchronously during the supply cycle of the purge gas.

In the other hand, a film is deposited by alernate supply of only a deposition gas and a purge gas without any reatanct gas into a reactor. In this case, the purge gas preferably contains constituent elements of a film material and does not react substantially react with the deposition gas if not activated; wherein plasma is preferably generated synchronously at least in part during the supply cycle of the purge gas to facilitate the reaction of the purge gas with the deposition gas.

The films deposited by above methods may be heat-treated after the deposition.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1A and FIG. 1B are drawings showing an apparatus for a chemical vapor deposition and a method of supplying reactant gases employed in a film deposition process of the prior art;

FIG. 2A to FIG. 2C are graphs showing a deposition process of the prior art which supply reactant gases in a time-divisional manner;

FIG. 3A to FIG. 3C are a schematic view of an apparatus to be employed to the present invention and graphs for illustrating a gas supplying method, respectively; and

FIG. 4A to FIG. 4C are drawings showing processes for forming a multi-component film by using the method of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiments of the present invention will be described hereinafter in reference to the appended drawings:

FIG. 3A is a schematic view of an apparatus to be employed to the present invention.

Referring to FIG. 3A, the apparatus is same as that of FIG. 1A, except that a plasma generator is attached thereto. RF(radio frequency) power is applied into a reactor 301 via an RF power supply 307 which is connected to a gas shower head 304 and a susceptor 302 so that plasma can be generated on a substrate 303. When RF power from the RF power supply 307 is cyclically applied into the reactor by turning on and off a switch 310 with the supply cycle of gases, plasma can be synchronously generated with the gas supply cycle. Gases are supplied through a supply tube 317, and the shower head 304 is adapted for the purpose of obtaining uniform flow 305 of process gases on the surface of the substrate 303 as in the prior art.

First embodiment of the present invention which is carried out by the apparatus shown in FIG. 3A will be described in reference to the graphs in FIG. 3B and FIG. 3C.

FIG. 3B is a graph showing that the process gases are supplied into the reactor in the supply cycle of deposition gas 13', purge gas 12', reactant gas 11' and purge gas 12'. At first, the deposition gas 13' is supplied into the reactor to be adsorbed to the substrate, and then the purge gas 12 is supplied to remove the remaining deposition gas from the reactor. Then, the reactant gas 11' is supplied into the reactor and at the same time the switch 310 is closed to activate the reactant gas 11' with plasma, and thus facilitate chemical reaction with the deposition gas 13'

adsorbed onto the substrate. When supply of the reactant gas is interrupted, the switch 310 is opened to stop plasma generation and the purge gas 12' is introduced to remove the remaining reactant gas. In this method, the film can be formed even if the reaction between the deposition gas 13' and reactant gas 11 is weak because the reactant gas 11 is activated with plasma.

For example, when a metal-organic compound is used as chemical vapor deposition source, plasma-activated reactant gas may accelerate decomposition of the metal-organic compound and reduce carbon contamination of the film. Also, the activation energy applied to the film by the plasma may enhance crystalization, physical characteristics and electrical characteristics of the film.

As a detailed example of this process, a copper compound may be reduced to form a metallic copper film. In the temperature no higher than thermal decomposition temperature of the deposition gas, chemical reaction between the deposition gas and hydrogen gas, i.e. the reactant gas, does not take place and thus a metallic copper film cannot be formed. Therefore, a plasma generator as shown in FIG. 3A is installed, and plasma is generated as hydrogen gas is supplied into the reactor so that chemical reaction between the hydrogen gas and the copper source adsorbed to the substrate surface may be accelerated and thus form a metallic copper film. If the plasma generator is powered on while supplying the deposition gas, the copper source may decompose in gas phase so that particle contamination or poor step coverage may take place. Therefore, it is advantageous to synchronize RF power applied to the plasma generator with the supply cycle in such a manner that the plasma generator is powered off when the deposition gas is supplied and on only when the reactant gas is supplied.

According to second embodiment of the present invention, a gas that may undergo a very weak chemical reaction with the deposition gas, if any, may be employed as a reactant gas or a purge gas, in condition that this gas contains constituent elements of the film. A gas supplying method like this is shown in FIG. 3C. In this method, the deposition gas 13' is primarily adsorbed to the substrate, the remaining deposition gas is removed by the purge gas 12' which undergoes almost no chemical reaction with the deposition gas, if any, but may include constituent elements of the film, and then the plasma generator is powered on to transform the

purge gas 12' into the reactant gas 15'. This reactant gas 15' can form a film by reacting with the deposition gas absorbed to the substrate. Then, after the plasma generator is powered off to stop the reaction, the deposition gas 13' can be supplied again into the reactor without any concerns about gaseous reaction. Therefore, during purge gas supply in the gas supply cycle, the plasma power supply is switched in the order of off, on, and off, thereby is equivalent of supplying a purge gas, a reactant gas and a purge gas, respectively. Also, the concentration of the activated species decreases very rapidly after the plasma power is turned off, so supply time of the purge gas can be minimized after the plasma power is off. In this kind of gas supply cycle, the gas-supply cycle consists of turn-on and turn-off of plasma generator instead of the supply of different gases. This method permits the time-divisional chemical vapor deposition with only two kinds of gases, so the gas supplying part of an appratus can be simple and the cycle time of gas supply can be reduced. Furthermore, the deposition gas and the purge gas do not react with each other even if mixed, so there is no concerns about the particle contamination in the exhausting part.

Both of the foregoing two embodiments can be employed for the deposition of TiN film which is used for diffusion barrier as well as adhesive and anti-reflectory coatings.

Using the first embodiment, a TiN film may be formed by repeating the cycle of the supply of Ti-organic source for a deposition gas, ammonia gas for a reactant gas, and nitrogen gas for a purge gas, in which plasma is generated when the reactant gas is supplied.

When employing the second embodiment, Ti-organic source is used for a deposition gas, nitrogen gas for a purge gas, respectively, in which the plasma generator is powered on thereby causing the absorbed deposition gas to react with nitrogen gas after the deposition gas is removed by nitrogen gas. A TiN film may be formed by repeating the cycle including these steps. In this case, the nitrogen purge gas never reacts with the deposition gas when the plasma power supply is off so that particle is not generated at all.

FIG. 4A to FIG. 4C are drawings showing steps of forming a multi-component film by employing a method of the present invention.

FIG. 4A illustrates a process of forming a single-component film 62 on the

substrate 66 by a simple process cycle. For example, a metal-organic source is chemisorbed to the substrate, and a reactant gas is supplied with plasma power turned on, and thus a film 62 is formed which contains the metal element contained in the metal-organic source.

FIG. 4B shows that the process of FIG. 4A is repeatedly applied to form different layers 62 and 63. Herein, a film is formed with a desired thickness and composition by alternatively forming layers 62, 63 with different composition which may contain different elements. The layers 62 and 63 can be as thin as an atomic layer, so the deposited film is sufficiently homogeneous, which may be transformed to thermodynamically more stable phase 65 after thermal treatment.

INDUSTRIAL APPLICABILITY

In the method of the present invention, a chemical vapor deposition of supplying process gases in a time-divisional manner is adapted with an idea of generating plasma synchronously with source supply cycle. Therefore, this method can be effectively applied for forming films which include metal components such as metal films, metal oxide films and metal nitride films which are used for semiconductor and flat panel display devices.

Herein above the invention has been described in reference to the preferred embodiments, but various other modifications and variations will be apparent to those skilled in the art without departing from the scope and spirit of the present invention.

Claims

WHAT IS CLAIMED IS :

1. A method of forming a thin film on a substrate by a chemical vapor deposition in which process gases are supplied into a reactor by repeating a cycle of time-divisional combination;

wherein said process gases include a deposition gas which forms a film when thermally decomposed but does not decompose thermally at the process temperature, a reactant gas which does not thermally decompose spontaneously at the process temperature or does not form a film upon thermal self-decomposition, and a purge gas for preventing chemical reaction between said deposition gas and said reactant gas; and

wherein plasma is generated on said substrate synchronously with at least one supply of said process gases in the cycle.

2. The method of forming a thin film according to claim 1, wherein plasma is generated synchronously with the supply of said reactant gases.

3. The method of forming a thin film according to claim 1, wherein said purge gas contains constituent elements of the film material and said reactant gas contains other constituent elements of the film material, respectively; wherein said purge gas does not react substantially with said reactant gas; and wherein said plasma is generated synchronously with the supply of said purge gas.

4. The method of forming a thin film according to claim 1, wherein said thin film is heat-treated after deposition.

5. A method of forming a thin film on a substrate in a chemical vapor deposition in which process gases are supplied into a reactor by repeating a cycle of time-divisional combination;

wherein said process gases include a deposition gas which forms a film when thermally decomposed but does not decompose thermally at the process temperature, and a purge gas for exhausting said deposition gas from a reactor;

wherein said purge gas contains constituent elements of the film material and

substantially does not react with said deposition gas in non-activated state; and

wherein plasma is generated synchronously at least in part with the supply of said purge gas causing said purge gas to react with said deposition gas.

6. The method of forming a thin film according to claim 5, wherein said thin film is heat-treated after deposition.

FIG. 1A

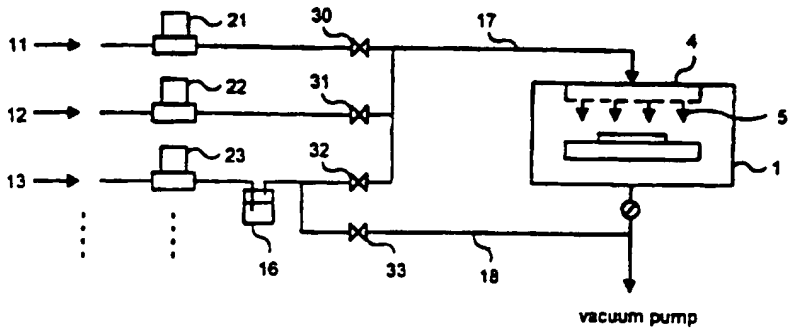

11
12
13
21
22
23
30
31
32
16
33
17
18
4
5
1
vacuum pump

FIG. 1B

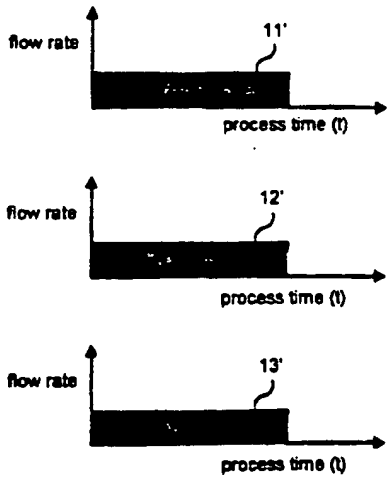

flow rate
11'
process time (t)
flow rate
12'
process time (t)
flow rate
13'
process time (t)

FIG. 2A

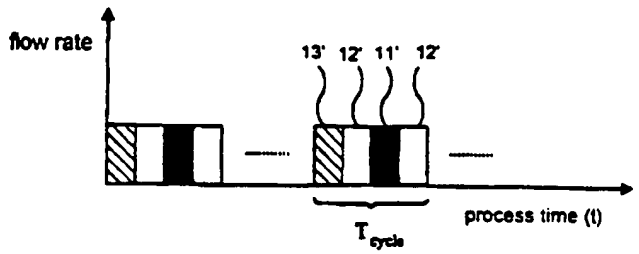


FIG. 2B

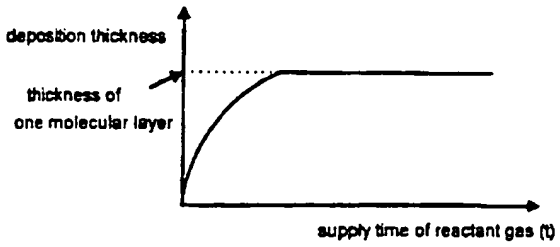


FIG. 2C

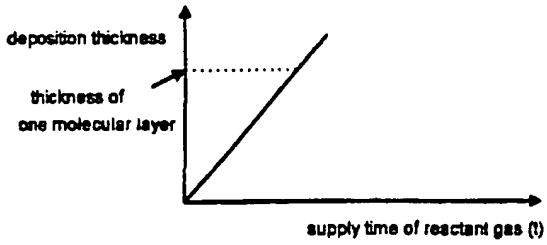


FIG. 3A

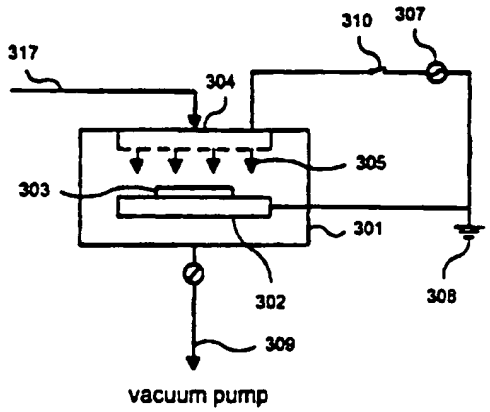


FIG. 3B

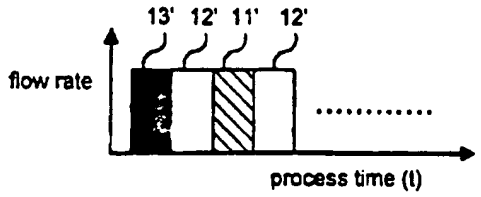


FIG. 3C

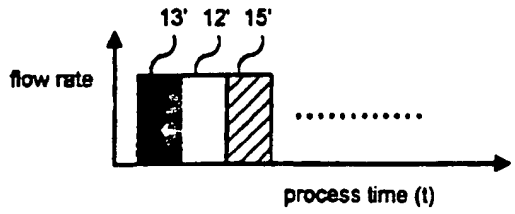


FIG. 4A

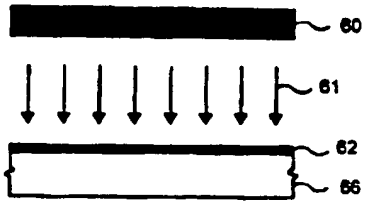


FIG. 4B

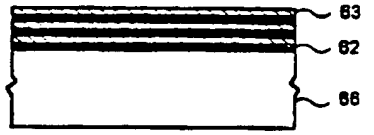
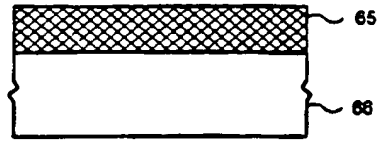


FIG. 4C



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/00310

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 H01L 21/205

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC7 H01L 21/205, IPC7 H01L 21/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fileds searched
Korean Patents and applications for inventions since 1975
Korean Utility models and application for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
KIPONET

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 06-291048 B1 (NISSAN ELECTRIC CO. LTD) 18.October.1994 (18.10.1994) page1, lines 1-10 claims 1 page 2, column 2, lines 38 - page3, column 1, lines 13 Fig. 1, Fig. 2	1-3
A	JP 03-048421 A (TOKYO ELECTRON LTD) 01. March.1991(01.03.1991) claims 1,2	1-3

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 JULY 2000 (19.07.2000)	19 JULY 2000 (19.07.2000)

Name and mailing address of the ISA/KR	Authorized officer
Korean Industrial Property Office Government Complex-Taejon, Dunsan-dong, So-ku, Taejon Metropolitan City 302-701, Republic of Korea	KIM, Jong Chan
Facsimile No. 82-42-472-7140	Telephone No 82-42-481-5722

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR00/00310

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 06291048 B1	18.10.1994	JP 2646941 JP 6291048	27.08.1997 18.10.1994

7

Form PCT/ISA/210 (patent family annex) (July 1998)

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: C23C 14/06, C23C 16/44	A3	(11) International Publication Number:	WO 00/16377
		(43) International Publication Date:	23 March 2000 (23.03.2000)

(21) International Application Number: PCT/KR99/00534

(22) International Filing Date: 10 September 1999 (10.09.1999)

(30) Priority Data:
1998-37257 10 September 1998 (10.09.1998) KR
1998-48993 16 November 1998 (16.11.1998) KR

(60) Parent Application or Grant
GENITECH CO., LTD. [/]; 0. YI, Kyoung-Soo [/]; 0. KOH, Won-Yong [/]; 0. KANG, Sang-Won [/]; 0. YI, Kyoung-Soo [/]; 0. KOH, Won-Yong [/]; 0. KANG, Sang-Won [/]; 0. HUH, Jin-Seok ; 0.

Published

(54) Title: METHOD FOR FORMING A THREE-COMPONENT NITRIDE FILM CONTAINING METAL AND SILICON

(54) Titre: PROCEDE POUR FORMER UN FILM DE NITRURE A TROIS COMPOSANTS CONTENANT DU METAL ET DU SILICIUM

(57) Abstract

A method for forming a three-component film containing metal, silicon and nitrogen for use in semiconductor devices on a substrate. The method of the present invention comprises the steps of: preparing separate reactive gases each including at least one selected from the group consisting of a gaseous metal compound, a gaseous silicon compound and an ammonia gas under conditions such that the gaseous metal compound and the ammonia gas does not form a mixture; determining a sequential gas supply cycle of the reactive gases so that supplies of the gaseous metal compound, the gaseous silicon compound and the ammonia gas are each included at least once within one gas supply cycle; and applying the reactive gases to the substrate by repeating the gas supply cycle at least once. According to the present invention, a three-component nitride film can be formed with a uniform thickness despite unevenness of a semiconductor substrate surface.

(57) Abrégé

L'invention concerne un procédé permettant de former un film à trois composants qui contient du métal, du silicium, et de l'azote, ce film étant destiné à être utilisé dans des dispositifs à semiconducteur placés sur un substrat. Le procédé de la présente invention consiste: à préparer des gaz réactifs séparés, chacun de ces gaz renfermant au moins un composé choisi dans le groupe constitué par un composé de métal gazeux, un composé de silicium gazeux, et un gaz ammoniacal, dans des conditions dans lesquelles ledit composé de métal gazeux et ledit gaz ammoniacal ne forment pas un mélange; à déterminer un cycle séquentiel d'alimentation de ces gaz réactifs de sorte que l'apport de chacun des composés de métal gazeux, de silicium gazeux, et de gaz ammoniacal s'effectue au moins lors d'un cycle d'alimentation; et enfin à appliquer ces gaz réactifs audit substrat, le cycle d'alimentation en gaz étant répété à une reprise au moins. Selon la présente invention, un film de nitrure à trois composants peut ainsi être formé, ce film présentant une épaisseur uniforme en dépit de l'aspect irrégulier de la surface du substrat à semiconducteur.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C23C 14/06, 16/44

A3

(11) International Publication Number: WO 00/16377

(43) International Publication Date: 23 March 2000 (23.03.00)

(21) International Application Number: PCT/KR99/00534

(22) International Filing Date: 10 September 1999 (10.09.99)

(30) Priority Data:
1998-37257 10 September 1998 (10.09.98) KR
1998-48993 16 November 1998 (16.11.98) KR

(71) Applicant *(for all designated States except US)*: GENITECH CO., LTD. [KR/KR]; 1694-5, Shinil-dong, Taedeok-gu, Taejon 306-230 (KR).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: YI, Kyoung-Soo [KR/KR]; 118-1506 Hanbit Apt., 99, Uheun-dong, Yusong-gu, Taejon 305-333 (KR). KOH, Won-Yong [KR/KR]; 105-605 Hanul Apt. 160-1, Shinsung-dong, Yusong-gu, Taejon 305-345 (KR). KANG, Sang-Won [KR/KR]; 133-1506 Hanbit Apt., 99, Uheun-dong, Yusong-gu, Taejon 305-333 (KR).

(74) Agent: HUH, Jin-Seok; J.S. Huh Patent Office, 206 Sungji Building, 1338-22, Seocho-dong, Seocho-ku, Seoul 137-070 (KR).

(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

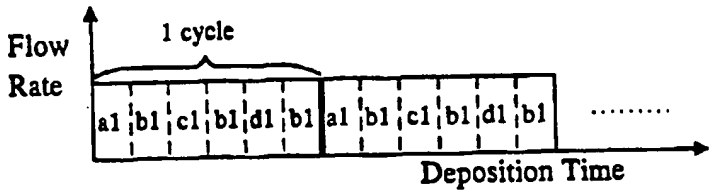
Published
With international search report.

(88) Date of publication of the international search report:
8 June 2000 (08.06.00)

(54) Title: METHOD FOR FORMING A THREE-COMPONENT NITRIDE FILM CONTAINING METAL AND SILICON

(57) Abstract

A method for forming a three-component film containing metal, silicon and nitrogen for use in semiconductor devices on a substrate. The method of the present invention comprises the steps of: preparing separate reactive gases each including at least one selected from the group consisting of a gaseous metal compound, a gaseous silicon compound and an ammonia gas under conditions such that the gaseous metal compound and the ammonia gas does not form a mixture; determining a sequential gas supply cycle of the reactive gases so that supplies of the gaseous metal compound, the gaseous silicon compound and the ammonia gas are each included at least once within one gas supply cycle; and applying the reactive gases to the substrate by repeating the gas supply cycle at least once. According to the present invention, a three-component nitride film can be formed with a uniform thickness despite unevenness of a semiconductor substrate surface.



a1 : Ar carrier gas bubbled in tetrakisdimethyamidotitanium

b1 : Ar gas

c1 : ammonia gas

d1 : silane gas

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00534

A. CLASSIFICATION OF SUBJECT MATTER

IPC[7]: C 23 C 14/06, 16/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[7]: C 23 C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

QUESTEL-WPI, EPO-WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 02-274867 A (SEIKO INSTR. INC.) 09 November 1990 (09.11.90) (abstract). [online] [retrieved on 11 February 2000 (11.02.00)]. Retrieved from: EPO WPI-Database.	1-18

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
„A" document defining the general state of the art which is not considered to be of particular relevance
„E" earlier application or patent but published on or after the international filing date
„L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
„O" document referring to an oral disclosure, use, exhibition or other means
„P" document published prior to the international filing date but later than the priority date claimed
„T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
„X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
„Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 February 2000 (11.02.00)	08 March 2000 (08.03.00)
Name and mailing adress of the ISA/AT Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Authorized officer Beck Telephone No. 1/53424/134

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00534

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP A2 2274867	09-11-1990	none	